THE ROLE OF ANTIMICROBIAL CLAY NANOFILLERS ON THE STRUCTURE AND DEGRADATION OF POLYCAPROLACTONE NANOCOMPOSITE FILMS: A COMPREHENSIVE STUDY

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INTRODUCTION

Currently, the big challenges and topics in the medical fields is the increasing incidence of resistant microbial infections.

Among the dynamically growing areas of material research is the development of *polymer nanocomposites*, as they play an important role in the field of antimicrobial materials for medical applications, because the surfaces of medical equipment and supplies are required to have sufficient antimicrobial properties, to be free of biofilm and to prevent such infectious surface transmission.

Addition of *nanofiller* leads to a two-way increase in the polymer nanocomposite activity, firstly by reinforcing the overall polymer structure and secondly acting as an active element against microbial infections. On the other hand, there is a polymer matrix, which, in view of the ever-increasing concerns about current environmental pollution, should be chosen from among *biodegradable polymers*. Therefore, hybrid nanocomposites, which are the result of the interaction between *clay minerals* and *biodegradable polymers*, appear to be very promising for these purposes.

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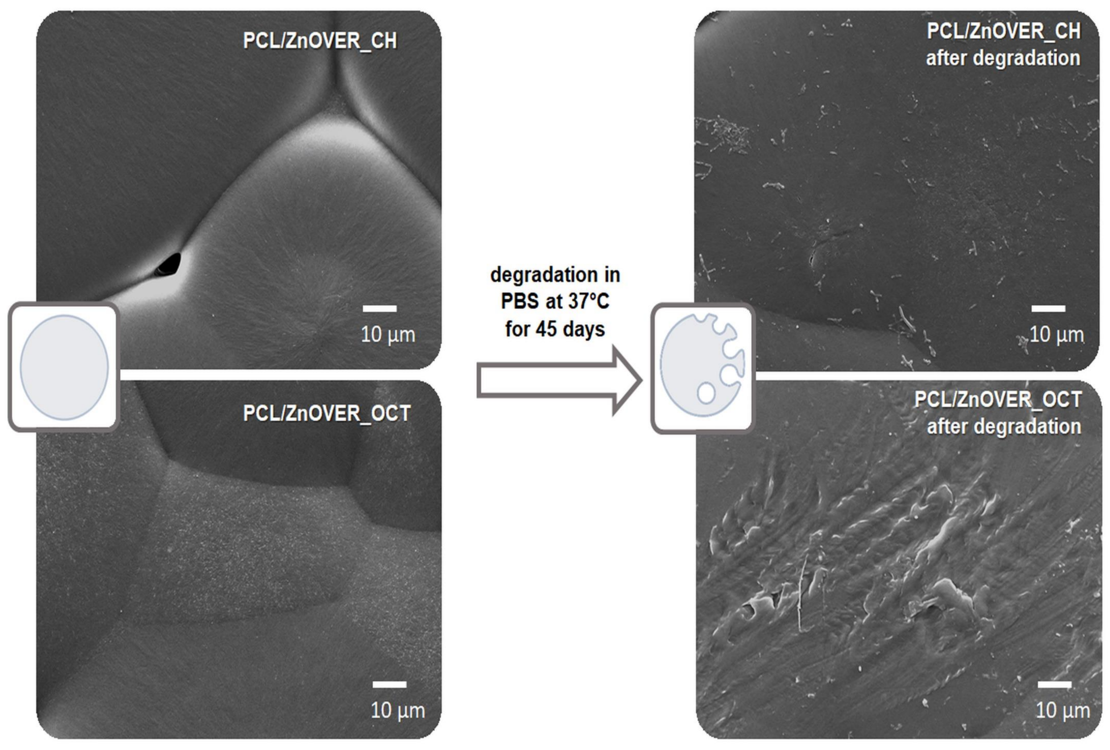


STRATEGY

Using clay nanofillers
antimicrobials chlorhexidine (CH) or octenidine (OCT) combined with ZnO anchored on vermiculite (VER)

Using biodegradable polymer
prepared novel PCL/clay nanocomposite films

We focused on the study of the effects of the nanofiller on the individual properties of the prepared polymer nanocomposites, from their mechanical, thermal, antimicrobial to degradation properties.

EXPERIMENTAL

Starting materials

- natural vermiculite VER, ZnO precursors
- chlorhexidine diacetate CH and octenidine dihydrochloride (OCT)

Preparation of ZnO clay nanofiller

- precursors ($ZnCl_2$, NaCl, Na_2CO_3) dissolved under 80°C, VER added
- sonicated 15 min, centrifuged, product dried, calcinated at 350°C
- resulted product named ZnOVER

Intercalation of antimicrobial agents

- clay water suspensions mixed with CH or OCT ethanolic solution
- stirred and heated at 75°C
- centrifuged, solid product dried overnight

Preparation of thin PCL/clay nanocomposite films

- 1g of PCL weighed into the beaker with 20 mL of chloroform
- beaker placed in an ultrasonic bath (UB) for 1 h
- 3 wt.% of the respective nanofiller were added (again 1h in UB)
- mixture in a thin layer poured onto a petri dish and dried at 40 °C

CHARACTERIZATION

- X-ray diffraction, FTIR spectroscopy
- Cumulative particle size distribution, ζ-potential measurements
- SEM microscopy, WCA
- Mechanical tests
- TGA, DSC

ANTIMICROBIAL ACTIVITY TEST

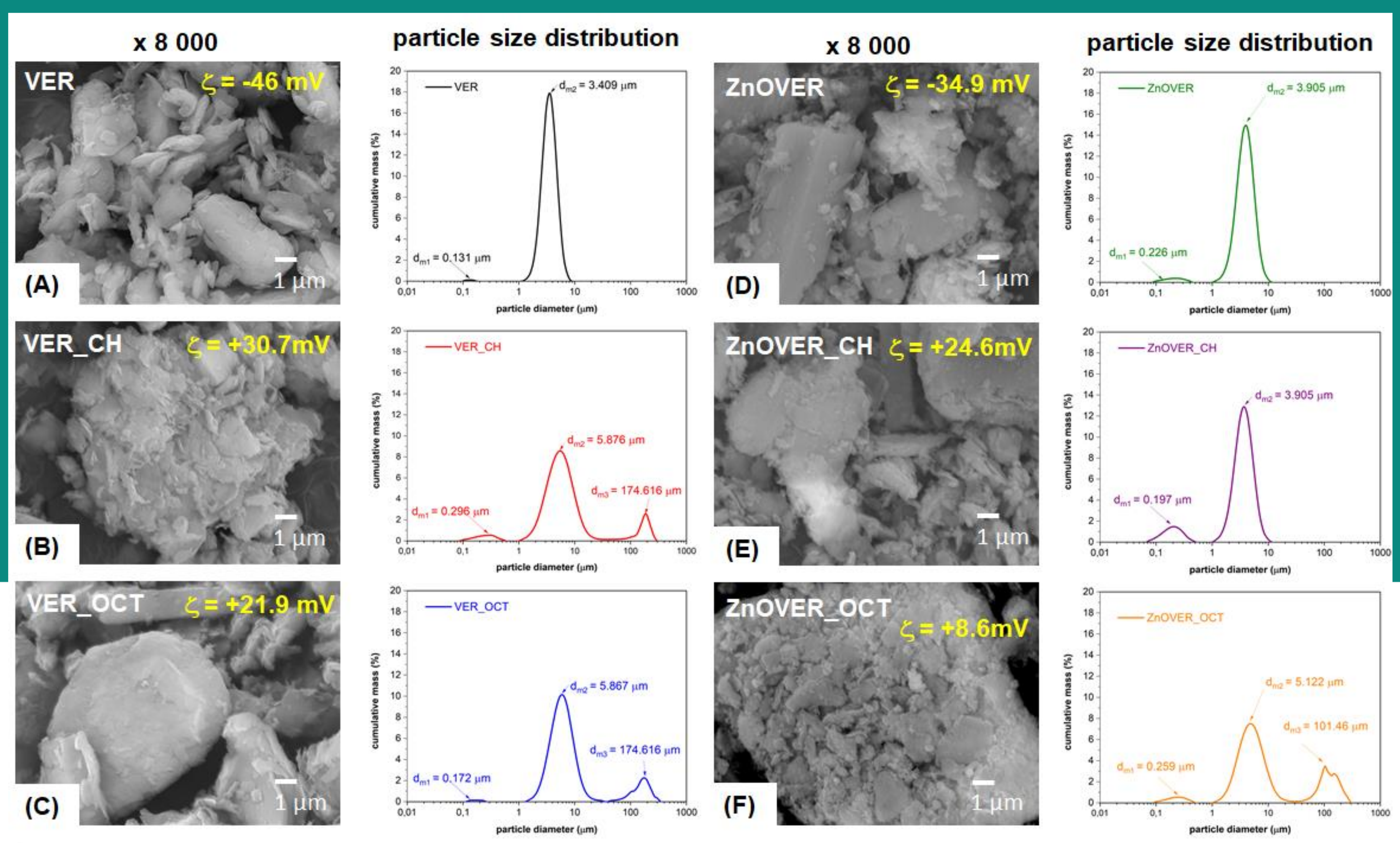
- CSN ISO 22196 (Measurement of Antibacterial Activity on Plastics and other Non-porous Surfaces)
- samples of size 1.5 x 1.5 cm
- bacteria suspensions 10^5 CFU/ml
  S. aureus (CCM 3953), *E. coli* (CCM3954)
- incubated after the elapse of 24, 48, 72 and 96 h

DEGRADATION ASSAY

- PCL nanocomposite films degraded according to ISO10993-13: Identification and quantification of degradation products from polymeric medical devices
- samples of size 2 x 2 cm, 10 mL of phosphate buffer saline (PBS, pH 7.4) and incubated at 37 °C for 5, 15, 30 and 45 days

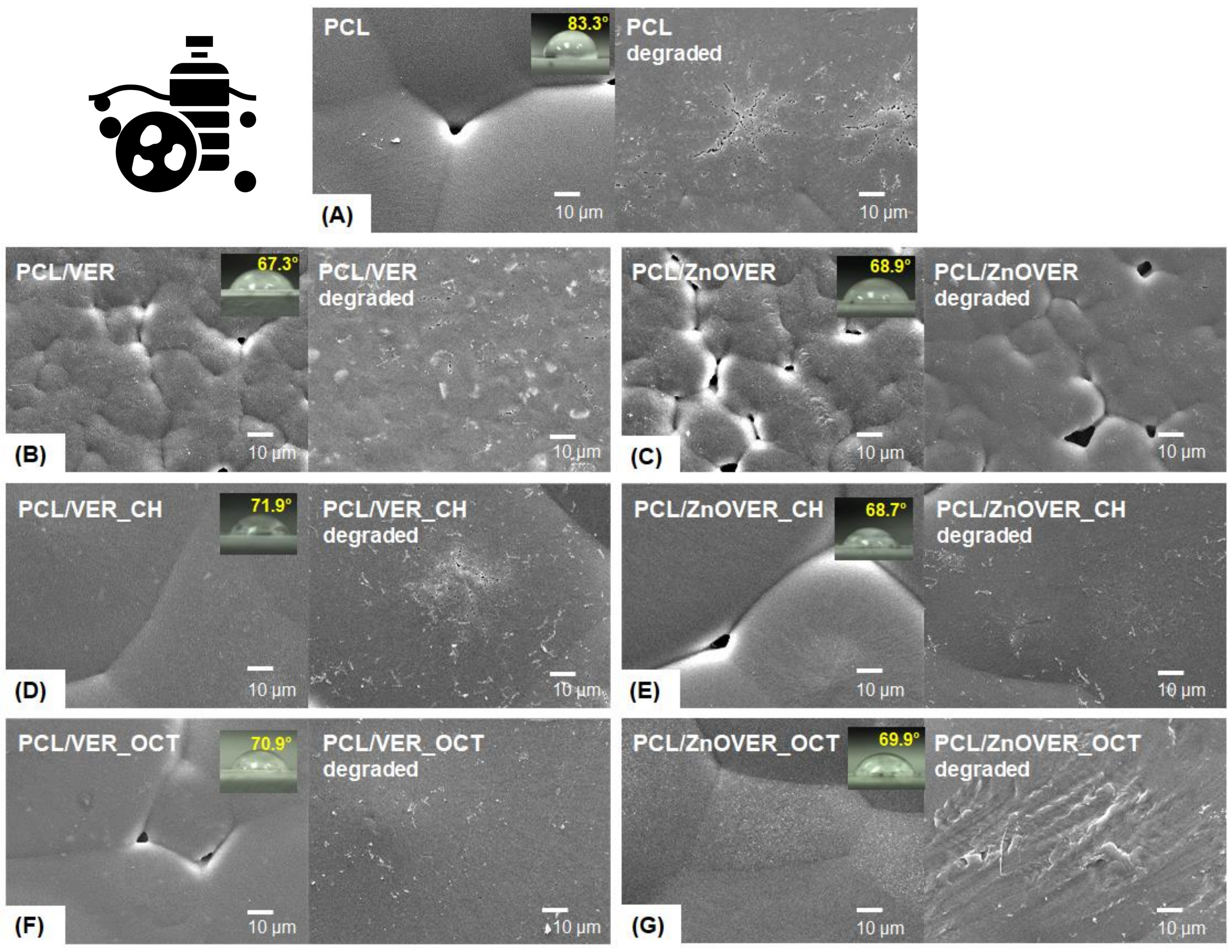
RESULTS

clay nanofillers



biodegradable thin polymer nanocomposites

Sample	Δ m (%)	T_{max} (°C)	E (MPa)	Rm (MPa)	S_{max} (mm/mm)
PCL	96.02	412.9	177.5	19.8	6.42
PCL/VER	95.71	410.1	187.3	14.3	4.16
PCL/ZnOVER	95.88	367.3	165.8	12.5	0.74
PCL/VER_CH	95.09	411.3	230.7	12.4	0.62
PCL/ZnOVER_CH	97.64	394.7	219.0	12.4	0.72
PCL/VER_OCT	94.78	413.6	213.2	14.1	0.94
PCL/ZnOVER_OCT	94.37	397.4	207.1	14.3	0.88



Sample	*S. aureus*			*E. coli*		
	A [lg]	time [h]	effectiveness	A [lg]	time [h]	effectiveness
PCL/ZnOVER	2.43	48	significant	2.21	48	significant
PCL/VER_CH	2.43	24		2.04	24	
PCL/VER_OCT	2.03	48		2.41	24	
PCL/ZnOVER_CH	2.43	24		2.41	24	
PCL/ZnOVER_OCT	2.01	24		2.41	24	

CONCLUSION

- clay nanofillers contained ZnO significantly decreases thermal and mechanical stability of prepared films
- nanofillers with the higher hydrophilic character are responsible for the faster degradation of PCL nanocomposite films
- films possessed high antimicrobial efficiency in long time intervals

Nacomposites for the possible application of such materials for the drug delivery with a long-term effect.

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